ISSN 0036-0244, Russian Journal of Physical Chemistry A, 2018, Vol. 92, No. 4, pp. 799–803. © Pleiades Publishing, Ltd., 2018.
Original Russian Text © M.R. Ibatullina, E.P. Zhil'tsova, S.S. Lukashenko, M.M. Anuar, M.P. Kutyreva, L.Ya. Zakharova, 2018, published in Zhurnal Fizicheskoi Khimii, 2018, Vol. 92, No. 4, pp. 659–664.

COLLOID CHEMISTRY AND ELECTROCHEMISTRY

Krafft Temperature of 1-Alkyl-4-Aza-1-Azoniabicyclo[2.2.2]octane Bromide Complexes with Transition Metal Salts

M. R. Ibatullina[a], E. P. Zhil'tsova[a,*], S. S. Lukashenko[a], M. M. Anuar[a], M. P. Kutyreva[b], and L. Ya. Zakharova[a]

[a] *Arbuzov Institute of Organic and Physical Chemistry, Russian Academy of Sciences, Kazan, 420029 Russia*

[b] *Kazan (Volga Region) Federal University, Kazan, 420008 Russia*

**e-mail: Zhiltsova@iopc.ru*

Received April 24, 2017

Abstract—The Krafft temperature (T_{Kr}) of 1-alkyl-4-aza-1-azoniabicyclo[2.2.2]octane bromides (Alk = n-C_nH_{2n+1}, n = 14, 16, 18) (D-n) and complexes of them with transition metals [Cu(II), Ni(II), Co(II), La(III)] in water is determined via conductometry and compared their corresponding acyclic analogs (alkyltrimethylammonium bromides). The dependence of the complexes' T_{Kr} on the structure of the inorganic salts and the hydrophobicity of ligands is established. It is shown that the complexation of D-n with metal nitrates and the shortening of the ligand hydrocarbon radical reduce T_{Kr}.

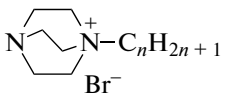
Keywords: cationic surfactants, transition metals, complexes, the Krafft temperature, conductometry

DOI: 10.1134/S0036024418040064

INTRODUCTION

It is known that the solubility of the ionic surfactants in water depends largely on temperature. Below the Krafft temperature (T_{Kr}), surfactants have very limited solubility, and it rises gradually along with an increase in temperature. Monomers and solid particles of a compound coexist in equilibrium in the solution, and the total solubility in the system is determined by the solubility of the monomers [1]. Micelles are form at the temperature where the concentration of dissolved monomers reaches the value of the critical micelle concentration (CMC). The solubility in the system starts to be determined by the solubility of aggregates, which is much higher than that of monomers. The equilibrium then shifts from solid particles toward micellar aggregates, solid particles dissolve, and equilibrium between monomers and micelles is reached in the solution. The concentration of monomers remains constant and is equal to the CMC. The solubility parameter corresponding to the state of the system where the solubility of monomers is the CMC and the hydrated solid compound transitions into the liquid micellar phase is known as the Krafft point. The temperature at which undissociated molecules are solubilized by micelles is the Krafft temperature [2, 3]. Since the solubility of surfactants increases sharply above the Krafft point, the Krafft temperature is an important surfactant characteristic that essentially determines the limits of applicability of solutions of an amphiphile.

Conductometry is one of the most widely used and convenient ways of determining the T_{Kr} of ionic surfactants [4]. We determined the Krafft temperature in water solutions of cationic surfactant with the bicyclic head group 1-hexadecyl-4-aza-1-azoniabicyclo[2.2.2]octane bromide (D-16) and complexes of it with Cu(II) bromide and transition metal [Cu(II), Ni(II), Co(II), La(III)] nitrates. To determine the role of the hydrophobic factor, we also studied solutions of 1-tetradecyl- and 1-octadecyl-4-aza-1-azoniabicyclo[2.2.2]octane bromides (D-14 and D-18 respectively) and complexes of them with lanthanum nitrate:



n = 14 (D-14)

n = 16 (D-16)

n = 18 (D-18)

It is known that a metal in an surfactant molecule can affect its physical and chemical properties [5–7]. The metallosurfactants we studied were micelle-forming compounds with elevated aggregation capacity, relative to (D-n) ligands [8, 9]. In addition, they had a wide range of properties useful in practice, including biological, solubilization, and transfection activity [8–10]. It was therefore important that we determine their physicochemical characteristics. The corresponding alkyltrimethylammonium bromides (tetradecyltrimethylammonium bromide (TTAB),